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PRESSURE ENFORCED FERROELECTRIC
TO ANTIFERROELECTRIC PHASE TRANSITION

PHILLIP E. HOUSER
PICATINNY ARSENAL
DOVER, NEW JERSEY

INTRODUCTION: Many fuzing systems require a setback-actuated power source which will produce a uniform output over a wide range of accelerations. In practice, a piezoelectric element is often used to generate the voltage, and mechanical shorting beams or zener diodes are used to regulate the voltage to a constant value.

The use of a material which undergoes a pressure enforced ferroelectric to antiferroelectric phase transition should result in a much less complex power source design. These materials are completely depolarized when they become antiferroelectric. Since the entire remanent polarization is released, the output is dependent only on the original polarization of the element, rather than on the pressure, as is the output of a conventional element. The use of an element of this sort in setback fuzes could eliminate rectifying and voltage regulating diodes and mechanical shorting beams as well as reduce the weight of the proof mass. Also, such an element could be used in a hydrostatic vessel as an improved impact power source of greater sensitivity from the standpoint of force or shock requirements as well as offering a multi-directional (graze) capability.

A material has been developed which appears to meet the requirements for a power source of this type. Minor compositional changes can effectively control temperature dependency in this material. Thus, once the effect of temperature on the various compositional modifications of this material has been determined, it will be possible to use the material with confidence over the entire military temperature range.

OBJECTIVE: The purpose of this project is to look into the pressure enforced ferroelectric to antiferroelectric phase transition as a charge release mechanism for use in fuzing. The main effort is to be directed at the effects of temperature, reverse voltage, and type of loading on compositions in the lead zirconate-lead titanate-lead stannate system containing small quantities of Nb_2O_5.

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The primary objective is to develop a material which will release a uniform charge output over a wide range of pressures, and over the entire military temperature range as a result of minimum applied pressure.

BACKGROUND: There are three basic mechanisms by which electric charge may be obtained from a polarized ferroelectric by the application of pressure: 1) Piezoelectric effects, 2) Domain reorientation effects, and 3) Depolarization due to phase transitions.

CHARGE RELEASE MECHANISMS: The piezoelectric effect dominates at pressures below 30,000 psi[1]. Piezoelectric charge release is due to a relative displacement of positive and negative ions as the material is strained[2]. So long as the elastic limit of the material is not exceeded, this process is reversible, and equal amounts of charge are released with application and with release of pressure (Figure 1).

In many perovskite ferroelectrics, domain reorientation effects become prominent as the pressure is increased to values between 30,000 and 75,000 psi. The charge output due to domain reorientation is additive with respect to the d_{33} output and produces a non-linearity in the output response[3]. The type of rotations possible depends on the crystallographic state of the material as shown by Figure 2.

Charge release due to a pressure enforced phase transition can only take place when the material is in a polarized ferroelectric state which is thermodynamically equal in energy to a non ferroelectric phase of smaller dimensions. In practice, these conditions are met by ferroelectric compositions very close to an antiferroelectric phase boundary[4].

In the lead zirconate-lead stannate-lead titanate system, Figure 3, the antiferroelectric phase is a tetragonal perovskite structure in which alternate rows of Ti^{+4} atoms are displaced in such a way that alternate dipoles are anti-parallel, e.g., 180^{0} apart. This structure has a net dipole moment of zero[5]. The ferroelectric phase is a rhombohedral structure which can easily be polarized to a net polarization of 20-35 microcculombs per square centimeter of electrode area[4].

When this material is switched from the ferroelectric to the antiferroelectric state, the net polarization is released, and appears as a charge on the electrodes of the element.

The background information collected indicates that the effect of elevated temperatures on the phase boundary has been determined for this compositional family. Also, room temperature output data is available for several of the compositions. The data available is insufficient for determining the effect of

temperature on the switching pressure, on the amount of charge output, or on the critical field strength. This temperature data will be required before these materials can be used in military devices. Therefore, a series of compositions which include the areas of the system expected to show the greatest temperature stability was selected for more intensive study.

PROCEDURE:
PRESSURE MEASUREMENTS: The hydrostatic measurements were made in a 100,000 psi vessel, equipped with six electrical feed-throughs, and a pressure transducer arranged in such a way that the electrical output of the specimen could be plotted continuously against pressure with an x-y recorder. Measurements can be made only at temperatures very close to room temperature with this system. A second pressure vessel was constructed for use at higher voltages, and over the military temperature range. Various pressure media were evaluated in this system, including RTV silicon rubber, FVC, and glass microbeads.

Axial loading measurements were made at pressures ranging up to 50,000 psi and at temperatures ranging from -50° to +70°C. Hardened steel anvils were used, and were well enough alined that the specimens were intact after being subjected to 50,000 psi.

High loading rates in which the entire charge output was built up in less than 1 microsecond were obtained using the setup shown in Figure 4. The element was cemented to the end of a 1/2 inch diameter brass rod. This rod was inserted into a mylar sleeve which was then inserted into a copper tube. The front of the element and the insulating mylar were both flush with the end of the tube. Nonconductive epoxy was used between the edge of the element and the outer tube. A layer of foil was placed over the end of the entire assembly to connect the front electrode of the element with the outer tube. A 1/16 inch thick aluminum projectile 1 inch in diameter was then fired at the end of the assembly with compressed air, at a velocity of 800 fps.

Slower loading rates with a rise time on the order of 3 microseconds were obtained with the sample holder shown in Figure 5. The best results were obtained with the specimen in the rear position, so that the shock wave had time to attenuate into a single smooth pulse. In this case, the sample holder was impacted with a 12 g projectile traveling at 1000 fps.

ELECTRICAL MEASUREMENTS: All systems for measuring electrical output vs. pressure were set up in such a way that an electrical output proportional to the pressure was available to drive an x-y recorder and give a continuous plot of output vs. pressure.
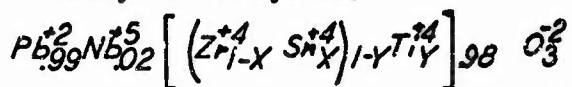
The short circuit measurements of charge output were made by feeding the output of the specimen into a Kintel Model 111-A operational amplifier which has been modified to act as an integrator.
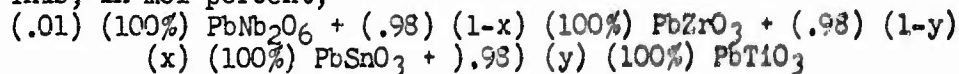
Measurements of charge output into a capacitive load were made by placing various sized capacitors in parallel with the test specimen, and measuring the voltage on the capacitor with a Keithley Model 200B electrometer with a 2000 volt attenuator. Field strengths across the specimens ranged from 2 volts/mil to 40 volts/mil, with the swamping capacitors used.

High voltage hysteresis loops were made at 60 hz and at approximately 1/2 cycle per minute. The measurements were made at field strengths on the order of 35 kv per centimeter. The circuits for both measurements are similar to the standard Sawyer-Tower circuit for measuring charge vs. electric field.

COMPOSITION: The specimens studied were polarized ferroelectric specimens close to the antiferroelectric phase boundary in the system.

$$Pb^{+2}_{.99}Nb^{+5}_{.02}\left[\left(Zr^{+4}_{1-x}\,Sn^{+4}_{x}\right)_{1-y}Ti^{+4}_{y}\right]_{.98}\,O^{-2}_{3}$$

Thus, in mol percent,
(.01) (100%) $PbNb_2O_6$ + (.98) (1-x) (100%) $PbZrO_3$ + (.98) (1-y)
      (x) (100%) $PbSnO_3$ +).98) (y) (100%) $PbTiO_3$

The composition was varied so that x = 0, 0.1, 0.2 and 0.3, and y = 0.04, 0.05, 0.06, and 0.07, th is, the composition contained up to 30% $PbSnO_3$, and up to 7% $PbTiO_3$. These compositions are shown in the phase diagram in Figure 3. The $PbSnO_3$ addition was made to control temperature effects[6], and the $PbTiO_3$ addition was made to shift the composition into a ferroelectric portion of the compositional system[7]. The $PbNb_2O_6$ content was held constant at 2 atomic percent Nb^{+2}, since this has been found sufficient to counteract the natural conductivity of the material[8]. The specimens were fabricated using conventional techniques and made up in disc form. Each disc was 1 mm thick by 1 cm in diameter, and had fired-on silver electrodes.

RESULTS AND DISCUSSION:
CHARGE RELEASE VS. HYDROSTATIC PRESSURE: Hydrostatic loading shows the greatest potential for making use of the pressure enforced phase transition, with the compositional family tested. Of primary interest is the charge output vs. pressure characteristics of these materials. In each case, relatively little charge is given off until a critical pressure is reached. When this pressure is reached, the entire remanent polarization is released over a very narrow pressure range, as Figure 6 shows. Further pressure increases produce only slight additional charge releases, and no

spontaneous repolarization of the specimen is noted upon release of pressure. The pressure at which the material depolarizes is dependent upon composition and temperature.

Compositions containing less than 10% $PbSnO_3$ were found to be very sensitive to slight changes in $PbTiO_3$ content. A 1% change in $PbTiO_3$ content changed the transition pressure by a factor of two. The compositions become less sensitive to change in $PbTiO_3$ content as $PbSnO_3$ content is increased, until at 30% $PbSnO_3$ (x=.3), the transition pressure is almost unaffected by slight changes in $PbTiO_3$ content. The relationships are shown in Figures 8 and 9.

The critical pressures for these materials range from 9,000 psi to approximately 50,000 psi. The materials which switch at 9,000 psi produce more charge at 9,000 psi than a conventional ferroelectric element produces at 50,000 psi.

CHARGE OUTPUT VS. ONE-DIMENSIONAL STRAIN: One-dimensional strain, e.g., axial loading, produced pressure charge curves which were nonlinear, as Figure 7 shows. The specimens were depolarized by the axial loading, and the composition with x = .2, y = .04 showed signs of a pressure enforced transition at 18,000 psi and -55°C. No transition was apparent with this composition at room temperature and, when tested at 60°C, the composition was found to be antiferroelectric, with no output. The composition with x = .3, y = .06 showed signs of the pressure enforced transition, but only at elevated temperatures. These two compositions are shown in Figure 11. Neither composition would be satisfactory for use in ordnance items because of temperature dependence. The remainder of the compositions appear to be depolarized by a domain reorientation process and produce the output curves similar to Figure 7. It had been hoped that it would be possible to produce the ferroelectric to antiferroelectric phase transition in these materials using axial loading. It now appears that the only compositions which can be switched in this manner are those that are so close to the anti-ferroelectric phase boundary that they have no long-term stability.

AIR GUN RESULTS: It was possible to completely depolarize the specimens in less than 1 microsecond by impacting them with projectiles accelerated with the air gun. The output obtained at these high loading rates was in excess of that obtained under static loading. The relative outputs of these materials under axial loading, hydrostatic loading, and when impacted with the air gun are shown in Figure 10.

HYSTERESIS LOOP MEASUREMENTS: The slow hysteresis loops give more information about the basic properties of a ferroelectric material than any other single measurement. Specimens which have low breakdown voltages or which become conductive are immediately identified, since they drive the recording system off scale.

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Antiferroelectric materials produce a linear figure with little hysteresis. Materials which are antiferroelectric but switch to a ferroelectric state under high electric fields produce a double loop.

The composition x = .2, y = .04 produced a conventional ferroelectric loop at room temperature when it was first tested. Cooling the specimen to -55°C produced no change. When the material was heated, it depolarized spontaneously at 40°C. At temperatures above 40°C, the material produced an antiferroelectric loop at field strengths below 25 kv/cm (Figure 12) and showed a field enforced antiferroelectric to ferroelectric phase transition at higher field strengths (Figure 13). This field enforced transition is easily identified by the characteristic double loops produced. When the material was cooled to room temperature, it continued to produce an antiferroelectric loop until the voltage was increased to a value in excess of E_c (Figure 14). The material then switched to the ferroelectric state and remained ferroelectric until again cycled to a high temperature. This is the composition which was found to have a pressure enforced transition under axial loading. In one case, the material gave no output since it had depolarized while in storage.

The composition x = .1, y = .05 became conductive at low temperatures. The cause of this conductivity has not been determined.

AXIAL LOADING: The charge output due to axial loading was measured by using a swamping capacitor which limited the field strength across the specimen to 1 kv/cm. All compositions show a considerable degree of temperature dependence. The compositions low in Sn content show the greatest temperature stability.

CONCLUSIONS: The mechanism of depolarization under axial loading appears to be that of domain switching rather than a ferroelectric to antiferroelectric phase transition.

Axial loading will depole the materials, however, the output is pressure dependent as saturation is not reached.

The compositions which have reasonably constant properties over the military temperature range have transition pressures of at least 30,000 psi.

Hydrostatic loading will be required in order to take full advantage of the constant output properties of these materials resulting from a rather abrupt ferroelectric antiferroelectric transition.
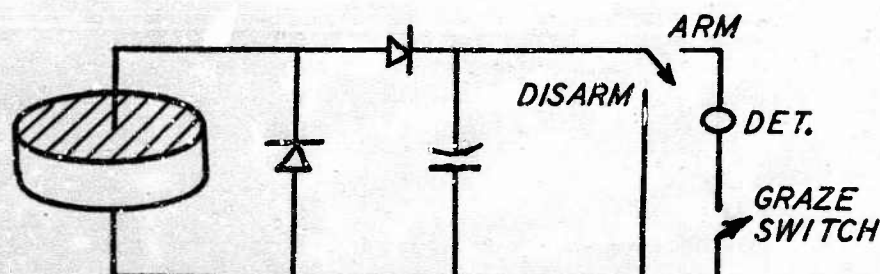
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FIG. 1 TYPICAL SETBACK ACTIVATED, GRAZE INITIATED FUZE.

Structure	BaTiO$_3$	PZT	Rotations	Polarization Direction
Cubic	above 120°C	above Curie point	---	X
Tetragonal	10°C to 120°C	More than 54% PbTiO$_3$	.90° 180°	cube edge
Orthorhombic	-75°C to 10°C	AFE State 0 to 5% PbTiO$_3$	60° 90° 120°	face diagonal
Rhombohedral	-200°C to -75°C	3% PbTiO$_3$ to 54%	71° 109°	body diagonal

FIG. 2 POSSIBLE DIRECTIONS OF POLARIZAION AVAILABLE FOR VARIOUS CRYSTAL STRUCTURES.
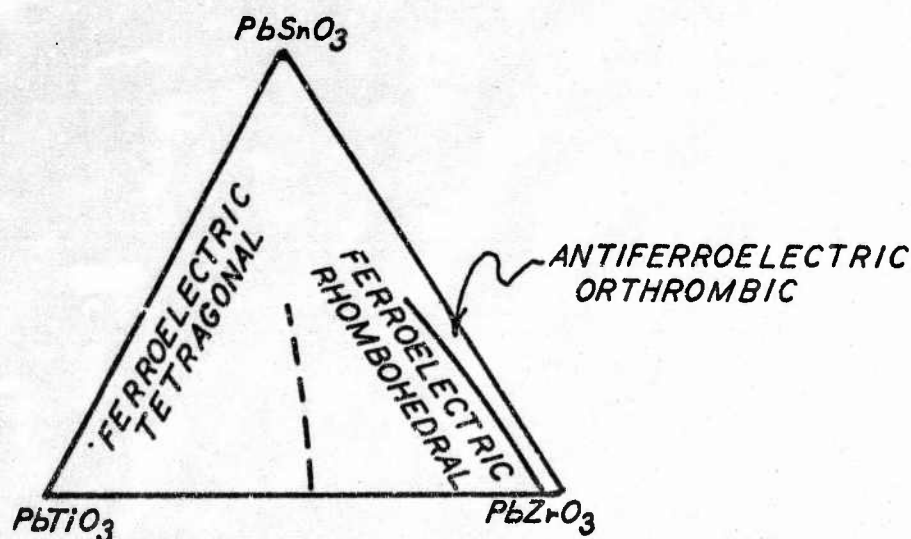
FIG. 3 MAJOR PHASES PRESENT IN SYSTEM PbTiO$_3$ PbSnO$_3$ - PbZrO$_3$
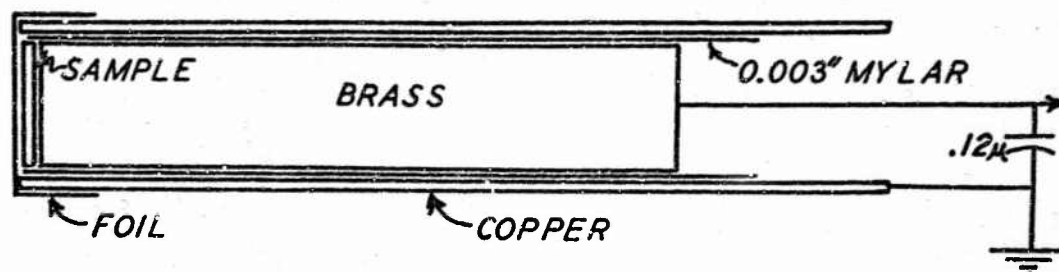
FIG.4. SAMPLE HOLDER USEDWITH AIRGUN FOR MEASURING ELECTRIC OUTPUT AT HIGH LOADING RATES. (1μ SEC. RISE TIME)
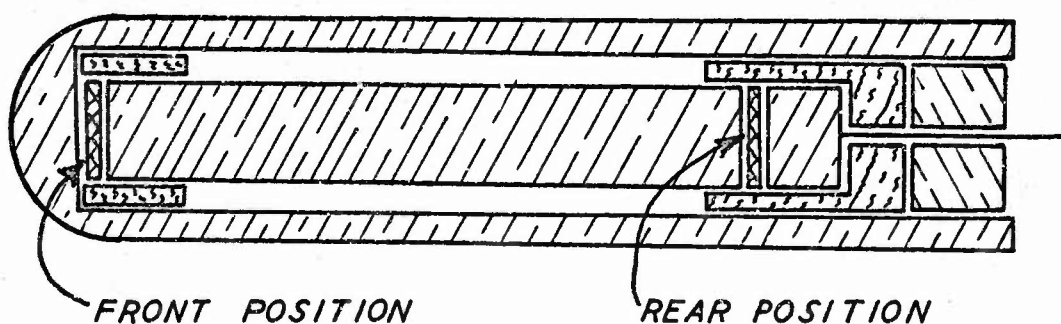
FIG. 5 AIRGUN SAMPLE HOLDER FOR 3μ SECOND RISE TIME LOADING.
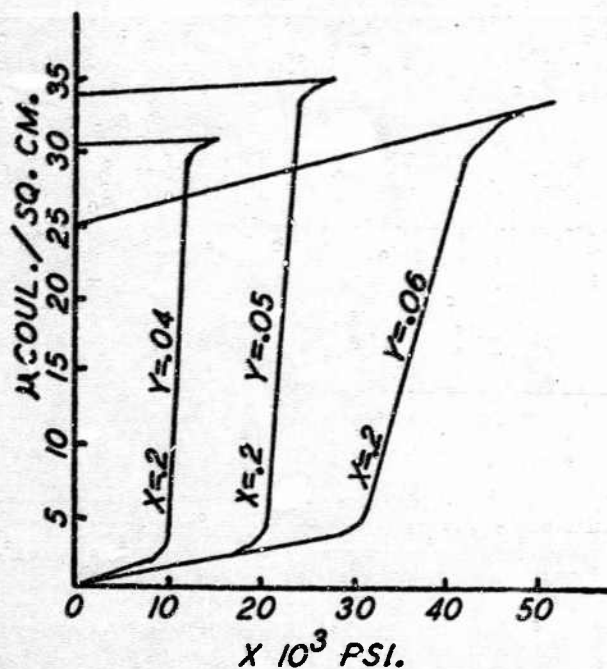
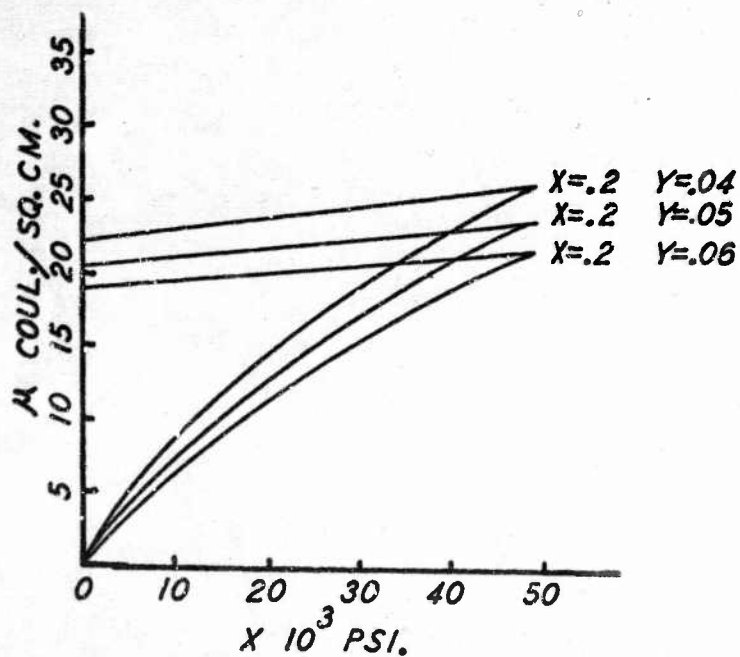**FIG.6** EFFECT OF COMPOSITION ON HYDROSTATIC TRANSITION PRESSURE.

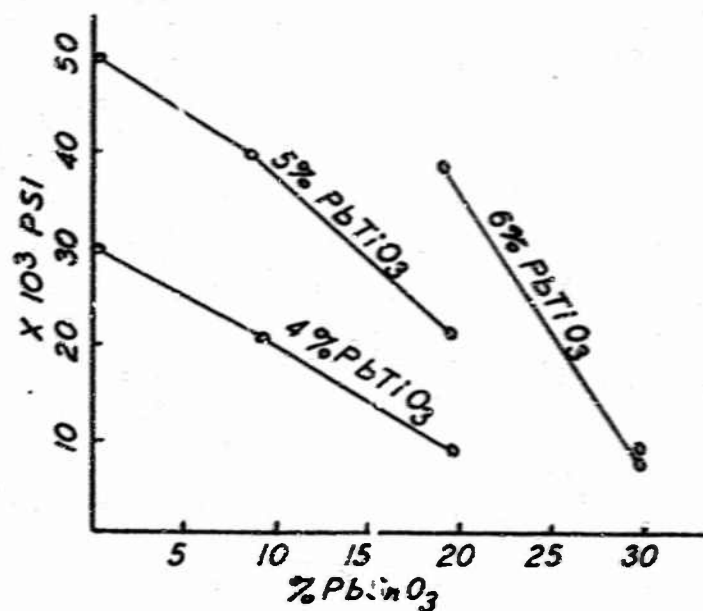**FIG.7** EFFECT OF COMPOSITION ON AXIAL TRANSITION PRESSURE.
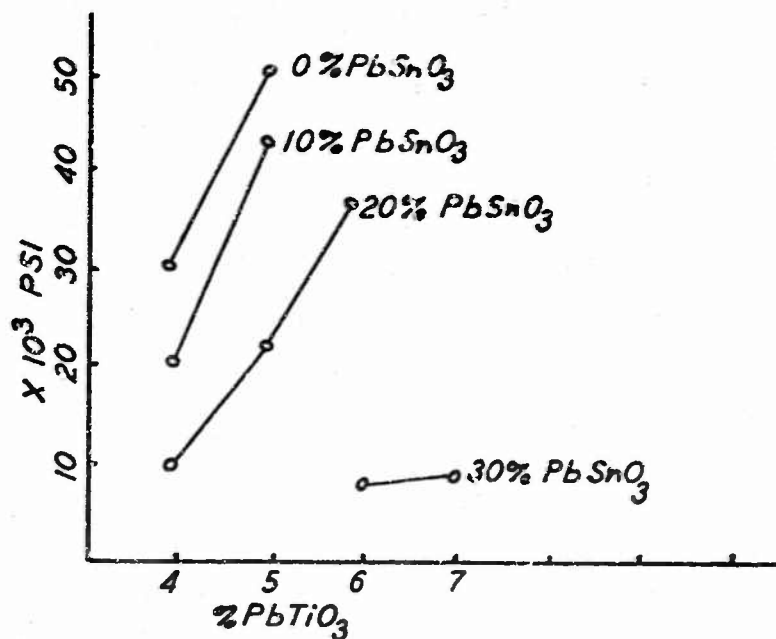
FIG.8 HYDROSTATIC TRANSITION PRESSURE VERSUS COMPOSITION.

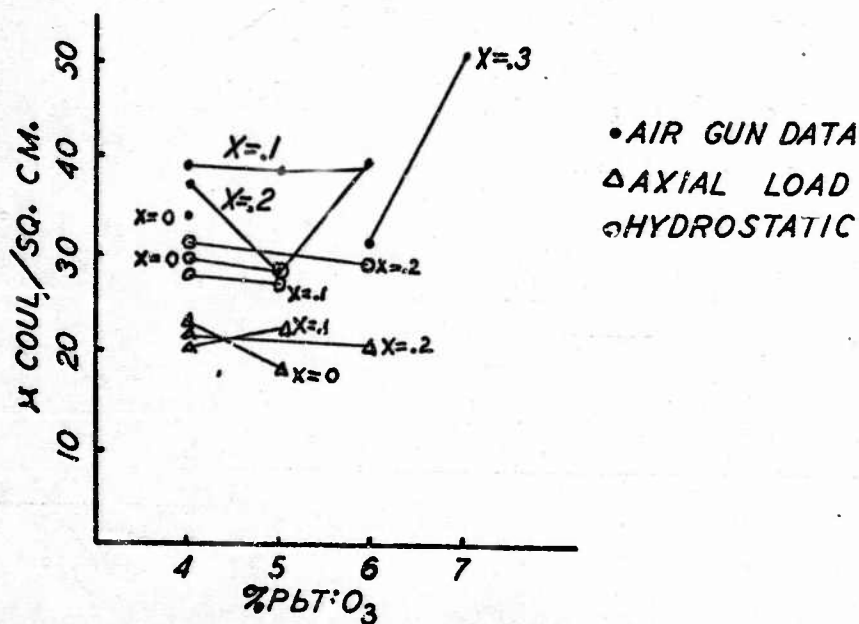FIG. 9. HYDROSTATIC TRANSITION PRESSURE VERSUS COMPOSITION
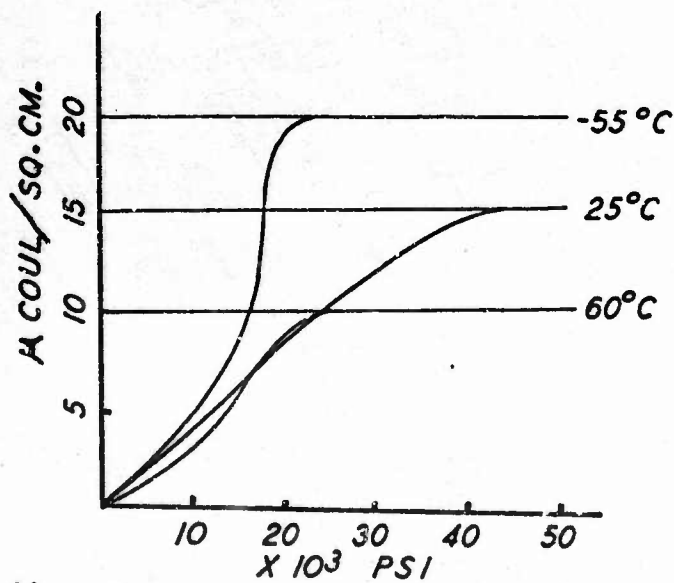
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FIG. 10 CHARGE OUTPUT VERSUS TYPE OF LOADING

FIG. 11 CHARGE OUTPUT VERSUS HYDROSTATIC LOADING
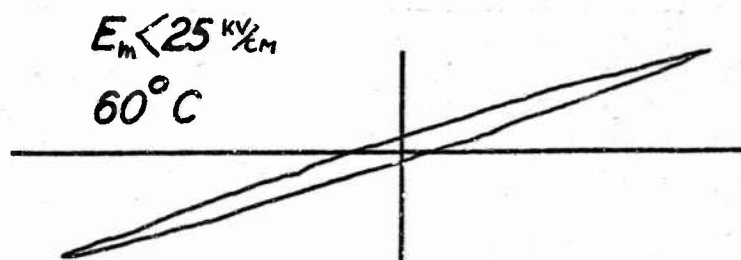AS A FUNCTION OF TEMPERATURE FOR X=.2 Y=.04

$E_m < 25\ ^{KV}/_{CM}$

$60°C$

FIG. 12 SLOW LOOP OF X=.2 Y=.04

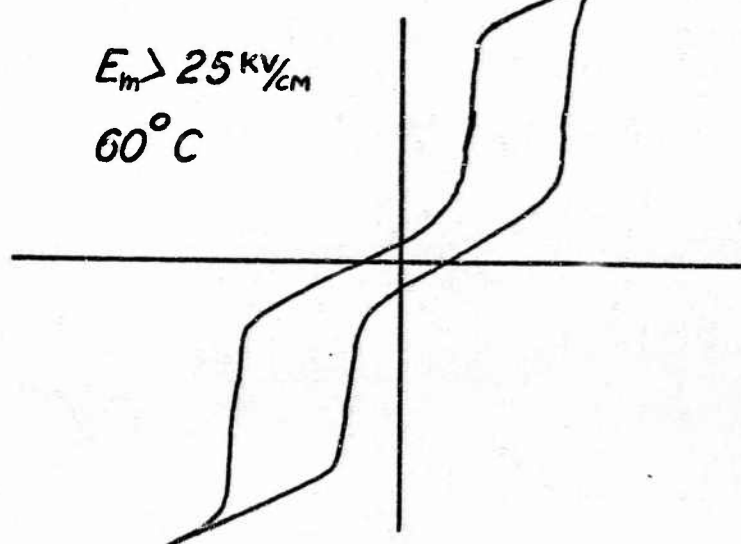$E_m > 25\ ^{KV}/_{CM}$
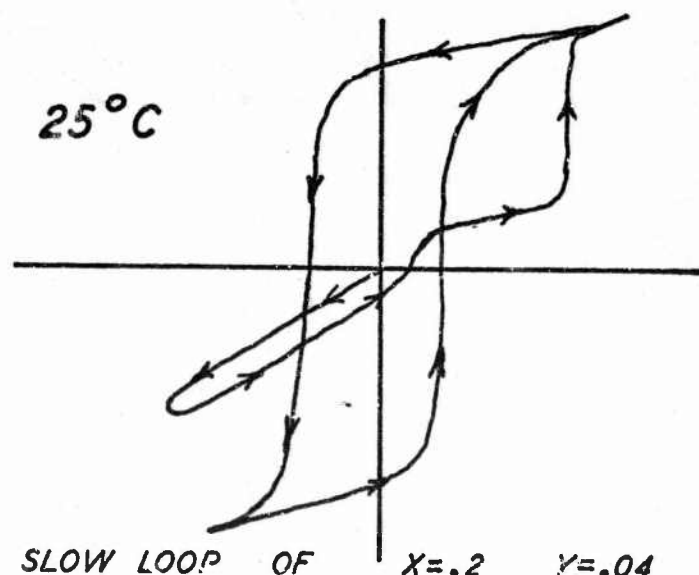
$60°C$

FIG. 13 SLOW LOOP OF X=.2 Y=.04

$25°C$

FIG. 14 SLOW LOOP OF X=.2 Y=.04

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